THE LUBRICITY PROPERTIES OF JET FUEL AS A FUNCTION OF COMPOSITION PART 1: METHOD DEVELOPMENT

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ABSTRACT

In recent years, the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of severe refinery processes in order to produce jet fuels of high thermal stability and cleanliness. Unfortunately, these processes remove naturally occurring polar material which impart a fuel's inherent lubricity. As a result, the lubricity properties of jet fuel products have decreased. This critical fuel property is essential for sustained high performance of fuel lubricated engine components. This paper describes a method that correlates naturally occurring and added carboxylic acids with fuel lubricity as measured by the Ball-on-Cylinder Lubricity Evaluator (BOCLE).

INTRODUCTION

In recent years, the quality of petroleum feedstocks has decreased. Thus, it has become necessary to employ severe refining processes in order to produce jet fuels of high thermal stability and cleanliness. Processes such as hydrotreating, hydrocracking, and clay filtering effectively remove the compounds which decrease thermal stability and hinder water removal by coalescence.[1-4] Unfortunately, some of these compounds are believed to impart a fuel's natural lubricity. Removal of these compounds, therefore, leads to a decrease in the operational lifetime of fuel lubricated engine components in some military and commercial aircraft. This in turn causes increased maintenance costs and down-time of aircraft. For the commercial airlines, this can cause a loss of revenue while an aircraft is grounded. For the military, this can lead to a decreased state of readiness.

Lubricity is a qualitative description of the relative abilities of two fluids, with the same viscosity, to limit wear and friction between moving metal surfaces.[2,4] It may be the most critical fuel property degraded by refinery processes.[5,6] There have been instances where the use of low lubricity fuel has caused loss of aircraft and human life.[7]

Considerable effort has been made in the development of a mechanical method which can be performed in the laboratory which will measure fuel lubricity. The current and most widely accepted method is the Ball-on-Cylinder Lubricity Evaluator (BOCLE). The lubricity of a fuel is determined by the measurement of a wear scar on a ball which has been in contact with a rotating cylinder partially immersed in a fuel sample. The reported value is the average of the major and the minor axes of the oval wear scar in millimeters. Typical values for jet fuels are between 0.45

and 0.95 mm.

This paper describes a method for estimating the lubricity properties of jet fuel by compositional analysis. The information developed by this technique is compared to measurements of the same fuels on the BOCLE. The method is based on a previously developed method for determining the concentration of corrosion inhibitor as a lubricity enhancer additive in fuel.[8-10] The analysis procedure involves a base extraction of a fuel sample with subsequent analysis by high resolution size exclusion chromatography. The amount of naturally occurring organic acids extracted from the fuels correlate well with their respective BOCLE measurements.

EXPERIMENTAL

Reagents- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. Six test fuels and a hydrocarbon standard used for BOCLE repeatability and reproducibility studies were obtained from the Naval Air Propulsion Center, Trenton, NJ. These samples included: two JP-4 fuels, one of which had been clay filtered; two Jet A fuels, one of which had been clay filtered; a JP-5 fuel; a JP-7 fuel; and ISOPAR M, an isoparaffinic fluid used as a low lubricity standard. A model JP-5 fuel was prepared using technical grade (99.7% purity) n-dodecane obtained from Phillips 66 Co. HPLC grade toluene was obtained from Burdick and Jackson Laboratories Inc. Other constituents of the model fuel were obtained from Fisher Scientific. These compounds included indan, decalin, t-butylbenzene, and cyclohexylbenzene. To investigate the effect of organic acid type on lubricity enhancement, the following acids were used: octanoic, decanoic, lauric, palmitic, stearic, cyclohexane carboxylic acid, and dodecylbenzene sulfonic acid.

Equipment and Materials- Samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30cm x 8.0mm I.D.). Uninhibited THF was used as the mobile phase. The THF was periodically sparged with dry nitrogen to inhibit formation of hazardous peroxides. The injector was a Rheodyne Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer for detection. Peaks were identified using a Varian Model 9176 strip chart recorder. A Fisher Accumet pH Meter Model 610A and a Fisher Standard Combination Electrode Catalog Number 13-639-90 were used for pH adjustments. BOCLE measurements were performed at twenty different laboratories worldwide. The BOCLE used was an InterAv Model BOC 100. The cylinders used were Timken Rings Part Number F25061 obtained from the Falex Corp., Aurora, IL. The test balls used were 12.7mm diameter, SKF Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

Method- Fuel samples were analyzed for organic acid concentration by a previously developed method.[8] For each sample, 100 ml were extracted with 100 ml of 0.2M aqueous sodium hydroxide. The aqueous phase was drained into a clean beaker and acidified dropwise with concentrated hydrochloric acid. The pH of the aqueous solution was lowered to 2.0 ± 0.03. The acidified aqueous phase was back-extracted with 100 ml HPLC grade methylene chloride. The methylene chloride was drained into a clean beaker and allowed to evaporate. After evaporation, the residue was dissolved in 2.0 ml HPLC grade THF and transferred to a glass vial with a teflon-lined cap.

BOCLE measurements on the seven fuel samples were performed in duplicate at twenty laboratories in the United States and Europe. The BOCLE method used was according to appendix Y of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.[11] The lubricity of each sample was measured using both a 500 and a 1000 gram load for the ball on cylinder. The compositional analysis data is correlated with the 500 gram load BOCLE data.

To determine the effect of sulfonic acid on lubricity enhancement, six model fuel samples were prepared for BOCLE analysis. These samples are listed with their relative wear scar diameter measurements in Table 1.

RESULTS

Figures 1 and 2 are size exclusion chromatograms for the seven fuel samples. Figure 1 represents those fuels which were determined to have high lubricity. Figure 2 represents those fuels which were found to have low lubricity. The region of interest on the chromatogram is the area where retention volume is between 5.25 ml and 7.5 ml. The peaks which elute after 7.5 ml are artifacts and were not extracted from the fuel. In Figures 1a and 1b, the peaks with retention volumes less than 6.25 ml correspond to the presence of the lubricity enhancer additive. The peak which elutes at approximately 5.85 ml represents the major active ingredient in most commercial additives, dilinoleic acid (DLA). It has a molecular weight of 562 daltons. This material is prepared by a 1,4-cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid. It possesses two carboxylic acid groups which are believed to be the points of adsorption to active surface sites.

The small peak which elutes at approximately 5.4 ml corresponds to the presence of trilinoleic acid (TLA). TLA, which is also a product of the Diels-Alder reaction, may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings. It has a molecular weight approximately three times that of linoleic acid (840 daltons).

The fuels whose chromatograms are depicted in Figures 1c and, Figures 2a through 2d, do not possess the lubricity enhancer additive. Their lubricity properties are, for the most part, solely related to the presence of naturally occurring carboxylic acids. The correlation of acidic materials present which elute at 7.25 ml is made with the BOCLE measurements. This retention volume was arbitrarily chosen because it was representative of naturally occurring organic acids present in each of the samples.

Table 2 lists the BOCLE results of the seven fuel samples. Statistically, it can be seen that there are two distinct groups. Three

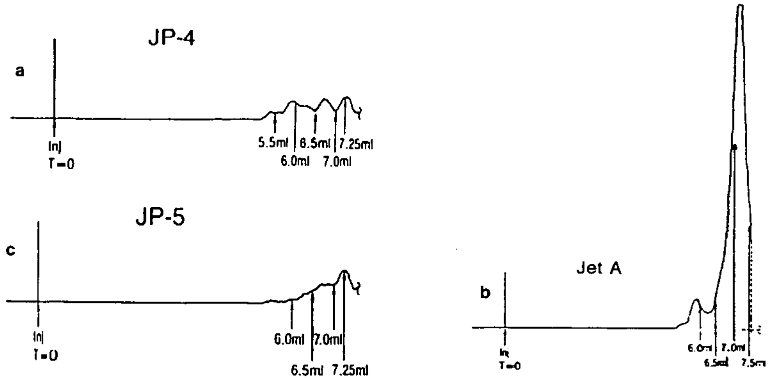

FIGURE 1: HPLC Chromatograms of High Lubricity Fuels as Determined by the Ball-on-Cylinder Lubricity Evaluator.

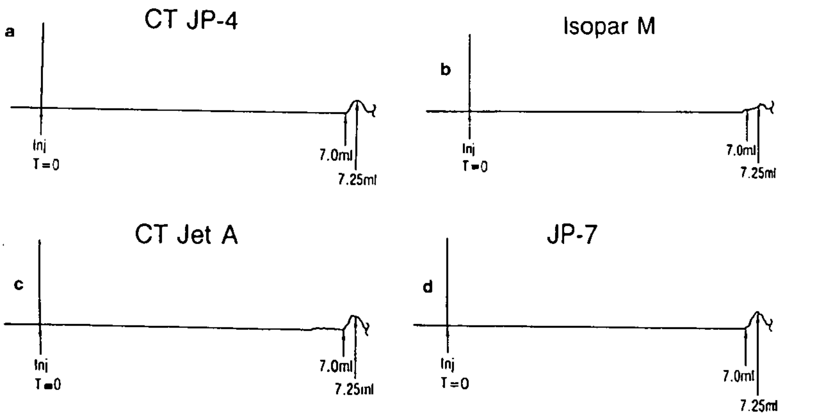

FIGURE 2: HPLC Chromatograms of Low Lubricity Fuels as Determined by the Ball-on-Cylinder Lubricity Evaluator.

fuels, JP-4, Jet A, and JP-5, were found to have high lubricity, and the four others, clay filtered JP-4, ISOPAR M, clay filtered Jet A, and JP-7, were found to have low lubricity. The results within each set are statistically the same. The average relative wear scar diameter for the high lubricity fuels is 0.64 mm ± 0.05 mm (7.8%). The average relative wear scar diameter for the low lubricity fuels is 0.94 ± 0.10 mm (10.6%). This implies that the precision of the BOCLE is better for high lubricity rather than low lubricity fuels.

Table 3 compares the the peak height at 7.25 ml with the BOCLE measurements for each of the fuels. Both JP-4 and Jet A possess the lubricity enhancer additive. It is, therefore, not surprising that these were high lubricity fuels. It can be seen in Figure 1b and Table 3 that the Jet A sample had a significantly higher concentration of the naturally occurring carboxylic acids and lubricity enhancer additive than either the JP-4 or JP-5. The lubricity of the Jet A, however, was not significantly higher than the other high lubricity fuels. Previous work has shown that there is a minimum possible wear scar diameter. The addition of more lubricity enhancer additive or the presence of a greater amount of naturally occurring lubricity enhancing species will not decrease the wear scar diameter.[11] In each of the high lubricity fuels, the maximum lubricity has been achieved. Thus, the lubricity measurements for these fuels are the same.

There may be some question as to why the JP-5 sample had significantly higher lubricity than the four low lubricity fuels. In Table 3, it can been seen that the JP-5 sample has only twice the concentration of acidic species eluting at 7.25 ml than the low lubricity fuels, yet the lubricity properties are significantly better. By comparison of Figure 1c with Figures 2a through 2d, it can be seen that each of the fuels in Figure 2 possess a single peak which elutes at 7.25 ml. The JP-5 sample depicted in Figure 1c has, not only this peak, but higher molecular weight acidic species which elute between 6.25 and 7.0 ml. We propose that the presence of these naturally occurring components in addition to two to three times the concentration of material eluting at 7.25 ml, yields the higher lubricity characteristics.

Dodecylbenzene sulfonic acid (DBSA) was found to have no effect on lubricity at concentrations that are normally found in jet fuel. Table 1 shows that at DBSA concentrations up to 1.0 ppm, DBSA did not decrease wear scar diameter measurements for the model fuel. This is in agreement with work performed by Lazarenko, et al. They found that corrosion inhibitors based on sulfonic acids did not increase jet fuel lubricity.[14] Model fuel doped with 96.0 ppm of a carboxylic acid mixture had, however, significantly lower wear scar diameter measurements, i.e., lubricity had increased as expected.

DISCUSSION AND CONCLUSIONS

The effect of long chain carboxylic acids on boundary lubriciation is well established. The presence of naturally occurring long chain carboxylic acids in jet fuel is believed to play a major role in lubricity enhancement. Any refinery procedure which removes these acids will have a detrimental effect on the lubricity of jet fuel products. Thus, processes such as hydrotreatment, hydrocracking, and clay filtration will decrease jet fuel lubricity.

It is well known that clay filtration adversely affects jet fuel lubricity. It has long been believed that this is a result of the removal of naturally occurring polar materials in fuel which impart lubricity.[2,3,7,12,13] The results of the BOCLE measurements confirm that lubricity does indeed decrease after clay filtration. The compositional changes can be seen by comparison of Figures 1b and 2c which represent Jet A fuel before and after clay filtration. The concentration of lubricity imparting organic acids has been drastically reduced. The lubricity enhancer additive has also been completely removed. The corresponding result is an extreme reduction in fuel lubricity. Comparison between clay filtered and non-clay filtered JP-4 cannot be made since these were two different fuels. It can be seen, however, that the mandatory corrosion inhibitor/lubricity enhancer additive is not present in the clay filtered sample.

This work has shown that a direct relationship between the presence of naturally occurring carboxylic acids and BOCLE measurements exists. Previous work by has also shown this relationship.[8] They analyzed a series of additive-free JP-5 and Jet A samples for naturally organic acids and correlated their presence with the fuels' respective BOCLE measurements. Additional work, which will be published in a subsequent paper, has shown the relationship in Naval JP-5 field samples as well as Air Force JP-4 field samples.

Sulfonic acids, however, were not found to influence BOCLE measurements and, therefore, do not enhance lubricity. Other polar material in jet fuel may contribute to lubricity enhancement. The carboxylic acids, which are well known surface active and lubricity enhancing species, are likely to be the major contributor.

In the future, it appears as though the BOCLE will be accepted as the standard method for measuring lubricity in the laboratory. The compositional analysis method can be used as a supplementary method to the BOCLE for verification of lubricity measurements. There are, however, a few advantages to the compositional analysis method over the BOCLE. First, the BOCLE is operator sensitive. Second, the instrument is sensitive to contamination of the fuels and test materials. Third, the presence of dissolved oxygen and water in a sample will influence the wear scar generated. Fourth, the BOCLE is very sensitive to relative humidity.

The compositional analysis method is not sensitive to relative humidity or dissolved oxygen and water in a fuel sample. Trace contamination between samples does not occur as readily with the compositional analysis method and its influence is significantly less. The compositional analysis method is also able to distinguish between three types of high lubricity fuel which the BOCLE cannot. These include; a high lubricity fuel without corrosion inhibitor, a high lubricity fuel with corrosion inhibitor, and a low lubricity fuel with corrosion inhibitor.

Although the lubricity enhancer additive is mandatory in U.S. military jet fuel, a number of Naval JP-5 fuel samples were indentified where the lubricity additive may not have been necessary. Addition of the lubricity enhancer additive to these fuels may have been an unnecessary expense. In addition, the lubricity enhancer additive has been shown to adversely effect the removal of water from fuel by coalescence. The use of the additive, therfore, may actually be detrimental rather than beneficial in some fuels.

Finally, for those fuels which have had the lubricity enhancer additive blended in at the refinery, the compositional analysis method can be used as a quality assurance and quality control procedure. Both the refiner and user can analyze a fuel for levels of both naturally occurring and added lubricity imparting organic acids.

TABLE 1

SAMPLE	Conc. DBSA (ppm)	Conc. R-COOH (ppm)	Normalized WSD
1	0.0	0.0	0.99
2	0.5	0.0	0.98
3	1.0	0.0	1.00
4	0.0	96.0	0.49
5	0.5	96.0	0.51
6	1.0	96.0	0.53

The Effect of Dodecylbenzene Sulfonic Acid on Lubricity as Measured by the BOCLE in the Presence and Absence of Carboxylic Acids.

TABLE 2

SAMPLE	Normalized WSD	± 2σ
JP-4	0.63	0.05
JET A	0.64	0.05
JP-5	0.65	0.05
CT JP-4	0.92	0.11
ISOPAR M	0.93	0.09
CT JET A	0.93	0.09
JP-7	1.00	0.11

The Lubricity of Fuel Samples as Measured by the Ball-on-Cylinder Lubricity Evaluator.

TABLE 3

SAMPLE	Normalized WSD	Pk Hgt @ 7.25 mL
JP-4*	0.63	10.0 mm
JET A*	0.64	≥165.0 mm
JP-5	0.65	**15.5 mm
CT JP-4	0.92	6.5 mm
ISOPAR M	0.93	4.5 mm
CT JET A	0.93	6.0 mm
JP-7	1.00	7.5 mm

*Contained a lubricity enhancer additive
**Higher molecular weight acidic species were also present

The Comparison of Organic Acid Composition at 7.25 mL Retention Volume with Lubricity as Measured by the Ball-on-Cylinder Lubricity Evaluator.

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